Carbon Analysis in Low-alloy and Carbon Steels with Handheld LIBS

Introduction

Presented here is a method to analyze carbon content in low alloy and carbon steels, utilizing the technique of handheld laser induced breakdown spectroscopy (HH LIBS). The method specifies the SciAps Z-200, the world’s only handheld analyzer capable of analyzing carbon content in alloys. The Z-200 uses a pulsed, 1064 nm laser, operating at 5.5 mJ/pulse and 50 Hz repetition rate. The onboard spectrometer spans 190 nm – 620 nm, with resolution < 0.13 nm in the 193 nm range of the carbon line utilized. The analyzer also uses an on-board, user replaceable argon purge gas. The argon canister, located in the handle, provides about 600 tests before requiring replacement.

The Carbon App Overview

The following is a list of features included with the Carbon App:

- Carbon calibration from 0-1% in carbon steels and low-alloy steels.
- ProfileBuilder desktop/tablet software for user-generated carbon calibrations on different bases or ranges.
- Full calibration in carbon- and low-alloy steels for other elements including Si, Al, Ti, V, Cr, Mn, (Fe by difference), Co, Ni, Cu, Nb, Mo, Pb.
- Carbon cal check and drift correction standards (3).

The Carbon App may be added to any existing Z-200 or Z-300 analyzer.

Performance Summary

Carbon data have been obtained from multiple analyzers, on carbon steels and low alloy steels (LAS) ranging from a pure iron (<0.005%) up to 1.2%. For properly ground materials, the test times for all analysis range between 15-22 seconds total, depending on the level of shot rejection performed by the method algorithm (more later). Users that are separating steels that differ by 0.2% carbon or more can generally complete tests in 10-15 seconds. The performance results are summarized in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value (% absolute)</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limit of Detection</td>
<td>0.12</td>
<td>3-sigma detection level for C in carbon and LA steels</td>
</tr>
<tr>
<td>Precision (absolute)</td>
<td>0.035</td>
<td></td>
</tr>
<tr>
<td>Accuracy</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Test time, Properly ground materials</td>
<td>9-12 sec. for 0.2% carbon delta</td>
<td>Includes pre-burn and purging time.</td>
</tr>
<tr>
<td></td>
<td>15-22 sec. for 0.1% carbon delta</td>
<td></td>
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</tbody>
</table>

Table 1. Summary Performance Parameters Z-200 for Carbon

The limit of detection of the current analyzer is 0.12% C, using the traditional 3-sigma rule for detection. Therefore this method should NOT be used to separate L and H grade stainless from standard grade stainless. The precision (repeatability) at any single carbon level was typically about ± 0.035% absolute, i.e. a 1030 steel with 0.30% C will yield a standard deviation of 0.035% C. The accuracy (bias) of any measurement can be as much as ± 0.1% for a properly calibrated Z-200.

Although the accuracy is specified as ± 0.1%, separation of steels that only differ by 0.1% is still possible. The accuracy quoted in Table 1 is for a global calibration spanning carbon steels, a range of low-alloy steels and Cr-Mo steels. The more expansive a calibration range, the less accuracy for any given alloy type.

The Z’s software supports multiple calibrations for specific carbon steel types. Reducing the range of steels in the calibration makes the analysis uncertainty more dominated by precision, rather than calibration-curve bias. To operate where precision dominates the measurement uncertainty, and thus in a way to separate alloys that differ by 0.1% carbon, users limit the calibration to a range of matrix-similar alloys. For example a user may easily create a calibration from the
global factory calibration that uses only carbon steels 1010, 1020, 1030, 1117, 1050, to achieve separation of 1020 from 1030, etc. Or the user may create a second type curve using low alloy steels such as 41XX’s, 4340, 4620 and 4820 to analyze 4130 from 4140. The analyzer software allows for use of multiple calibration curves, and easy switching between curves.

**Calibration and Precision Data:**

The global calibration curve is shown in Figure 1. As with spark OES, the calibration ratios the 193.1 nm carbon intensity to the intensity of a nearby Fe line. The calibration is then a fit of known C assays to the intensity ratio of carbon to iron. The global curve uses a range of carbon steels 10XX, an 1117, plus several LAS including 41XX, 43XX, 46XX, and 86XX. The Z-200, when equipped with the Carbon App, will be factory calibrated with the global carbon curve referenced above. In general, use of the global curve is acceptable for basic separation of carbon steels that differ by 0.2% C or more.

**Calibration to Carbon Steel Sub-types, When to Use it:**

For more precise sorting of carbon steels — those that differ by as little as 0.1% C — we recommend limiting the calibration curve to a family of alloys that encompass the steels of interest. For example to separate a series of carbon steels such as 1010, 1020 and 1030, modify the global calibration curve by turning off the low-alloy steels, and maintaining only carbon steels in this concentration range of interest. For example Figure 2a displays a specific carbon steel calibration starting with the global factory carbon calibration, then limiting it to carbon steels from 0 - 0.5%. As shown, with this more type-specific curve, the Z-200 will then yield reliable separation of these carbon steels, such as separating a 1020 from a 1030 or an A106 from 1018 or 1040.

**Two Important Notes:**

- We always recommend using at least 4 calibration points (iron blank can be one) and a linear fit. This prevents artifacts from incomplete sample prep from biasing the calibration. If an incorrectly prepped calibration sample is included, it will not lie on a straight line fit.
- SciAps does not recommend attempting to separate carbon steels that differ by less than 0.1% carbon.
Handheld XRF operators may attempt to separate 4130 from 4140 based on the Mn content. This can be risky because of the large Fe interference present with XRF. Even slight drift or surface contamination can skew the Mn result in either direction. The Z offers a way to measure BOTH the Mn and the C content, for a more confident analysis of these alloys.

Tables 2 and 3, respectively show repeatability of results for 4130 and 4140 low-alloy steels. Assayed carbon content is 0.29% for 4130 and 0.41% C for 4140.

As a second example consider to separate 4130 from 4140. Starting with the global curve in the calibration software (Profile-Builder), the user can create a new calibration curve by enabling only the 4130, 4140, 4620, 8620, plus a few other low alloy steels with carbon range from blank to 0.5%. The calibration curve is shown in Figure 2b. Repeatability data for both 4130 and 4140 is shown in Tables 2 and 3 respectively, demonstrating the clear ability to reliably separate these two common low alloy steels by their difference in carbon content.

### Case Study:
Separate 4130 from 4140 Low Alloy Steels

As a second example consider to separate 4130 from 4140. Starting with the global curve in the calibration software (Profile-Builder), the user can create a new calibration curve by enabling only the 4130, 4140, 4620, 8620, plus a few other low alloy steels with carbon range from blank to 0.5%. The calibration curve is shown in Figure 2b. Repeatability data for both 4130 and 4140 is shown in Tables 2 and 3 respectively, demonstrating the clear ability to reliably separate these two common low alloy steels by their difference in carbon content.

### Carbon Steel Example:

Precision data for carbon steels A108 (0.15% C) and 1030 (0.331% C) are shown in Tables 4, 5. Precision and relative standard deviation are comparable to the low alloy steels. Again, using a more limited curve allows separation of carbon content in alloys that differ by approximately 0.1% or more.

### Single-standard Type Calibration:

The Carbon App does not currently support single alloy type standardization. A surface prep artifact (i.e. improper grinding) may be incorporated into the type standard when testing it. If other pieces of the same alloy material are ground differently, they may fail to be properly identified, despite being the same alloy. Our studies leading to this method validate that a minimum 4-point calibration with a linear fit are satisfactory to expose improper sample preparation.

### Analysis of Real-world Materials:

As part of the field testing of this new carbon method, materials from several real-world applications were tested. Shown here are results from some refinery piping provided by a major refining company. These components were previously in-service components and are common A108 and 1010 common carbon steel alloys. They were prepped according to the grinding method described later, and analyzed with the same testing procedure. The same carbon steel calibration shown in Fig. 2a was utilized for these materials. The real-world carbon steel measurements performed similar to the reference material tests.
There are four steels that contain carbon concentrations 0.073%, 0.12%, 0.18% and 0.23%. Figure 3 shows the results of the Z-200 LIBS data versus the assayed data. Tables 6 and 7 show repeatability data for the 0.12% and 0.18% carbon contents. Repeatability on the other two samples were comparable, and omitted for brevity. These results on actual refinery piping are comparable to the data from reference materials. Carbon steels that differ by 0.1% carbon or more are easily separated such as 0.073 and 0.18 or 0.12 and 0.23% carbon. In fact we show the results for the 0.12% and 0.18% steels to demonstrate that even with good precision (± 0.02% carbon, good for a handheld device), when considering the precision band, you cannot separate these two alloys.

Method

The analysis method requires sample preparation with a handheld grinder, followed by testing with the Z-200. The Milwaukee M12 grinder and R980 quick change discs were used for the data collected during this app development.

Definitions:

A test means a single test of the material with the Z LIBS analyzer. A result is a final answer that consists of five (5) valid LIBS tests which are automatically averaged by the analyzer software. Each test takes 3 seconds, so a result is typically 15 seconds due to the 5-test average. If the software rejects one or two of the tests based on built in data quality rejection criteria, a result may require up to 22 seconds. These times are required to achieve carbon separations that differ by 0.1% carbon.

A TEST is defined as a single analysis on the material, consisting of preburn and spectral data from 6 different raster locations. A test showing the six laser burns in the material is shown in Fig. 5.

A RESULT is defined as an average of 5 valid tests. A result shows the measured percent carbon and the measurement uncertainty.

The testing works as follows. The operator performs five tests on the ground material, which the analyzer software automatically averages for a final result. The built-in rejection algorithm may reject one or more tests, thus requiring a total of 6 or 7 total tests to get an average of 5 good tests. If more than 1 or 2 tests are rejected, the material wasn’t properly ground and should be re-ground.

The rejection algorithm takes advantage of the 2D rastering of the laser performed by the Z-series analyzer. For each test, the laser is rastered to six discrete positions on the material, spaced about 200 um apart. The sample is pre-burned at each location for 0.2 sec, spectral intensity data gathered for 0.3 seconds per position (for a total of 0.5 seconds per location). The software rejects any test where the standard deviation is above a factory preset threshold. The software prompts the user for additional tests until the required 5 good tests are achieved and averaged for a result.

A high carbon uncertainty from a test indicates improper sample grinding. In these cases, the laser has likely struck a region with high carbon surface contamination that was not removed by grinding. If the resulting test is not rejected, then the overall result will be biased high. If zero or perhaps one test is rejected during a carbon measurement, then the sample was properly ground.

The test rejection criteria built into the SciAps Carbon App provides a reliable quality indicator that the sample material was properly prepared.

Summary

The SciAps Z-200 or Z-300 are handheld LIBS analyzers that now offer carbon concentration measurements in carbon steels and low-alloy steels. The method requires sample grinding using a specified handheld grinder, followed by a (typical) 15 sec test with the Z. The testing time includes pre-burn and purging time. Provided operators follow the procedures described, the Z will allow carbon steel grades that differ by 0.1% C or more to be reliably separated. The Z uses a data rejection algorithm to assure proper grinding, and argon purge to achieve the required precision. Consistently good sample prep and argon purge are critical for carbon analysis with HH LIBS.